Journal of the American Oil Chemists' Society **Surfactants & Detergents**

Technical

Effect of Surfactant Structure on Stability of Enzymes Formulated into Laundry Liquids

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ABSTRACT

The effect of surfactant structure on enzyme stability in heavy duty laundry liquids was investigated. Surfactants studied were alcohol ethoxylates and anionic surfactants having varying hydrophobic and hydrophilic types and chain lengths. Enzymes used were proteases and amylases. The results showed these enzymes were considerably more stable when formulated into laundry liquids containing alcohol ethoxylates and ethoxysulfates than when formulated with alcohol sulfates and surfactants containing sulfonate groups such as linear alkylbenzene sulfonates and alpha olefin sulfonates. Enzyme stabilizer systems were only partially effective in reducing the enzyme-deactivating influence of sulfonate-containing surfactants.

INTRODUCTION

Enzymes have been used in laundry detergents for over 50 years, originating in Germany in the early 1930's (1). These enzymes were mostly proteolytic-attacking proteinaceous material arising from stains such as blood and milk. In the U.S., enzymes achieved significant growth in the 1960's in laundry powders but lost market share due to the dusting problems experienced in detergent manufacturing plants and the resulting health questions raised. However, enzyme encapsulation techniques have minimized toxic effects from enzymes, and they are used safely today both in detergent manufacturing plants and in home consumption. The safe use of enzymes in laundry detergents has led to incorporation of enzymes in well over 50% of all laundry detergents used in Europe.

Although enzymes are not used as extensively in laundry products in the U.S. today as they are in Europe, they were reintroduced into some U.S. laundry powders in the late 1970's. Over the past several years, enzyme growth in the U.S. has been greatest in the unbuilt laundry liquid sector where both proteolytic and amylolytic enzymes have appeared. Two major factors have been responsible for this growth. First, use of laundry liquids themselves grew significantly over the past 15 years, to about 25% of the household laundry market, mostly as a result of decreased phosphate use in detergents. Second, energy saving considerations have resulted in lower washwater temperatures, prompting a search for additives like enzymes which can compensate for poorer performance at cooler temperatures (2,3).

The use of enzymes in laundry liquids reduced the possible residual dusting problems posed by granulated enzymes in laundry powders. However, this new use creates the problem of enzyme shelf stability in an aqueous medium. The presence of water tends to accelerate the rate of enzyme deactivation. In addition, the choice of a proper surfactant

Presented at the AOCS meeting in Dallas, May, 1984.

becomes critical in an aqueous environment, because the surfactant system and the enzyme have the capability of interacting. If the surfactant is deactivating, as for example dodecyl sulfate (4,5), enzyme deactivation can proceed at a more rapid rate, making it difficult to obtain a liquid product in which the enzyme has a reasonable shelf life.

The major surfactants used in U.S. laundry liquids are alcohol ethoxylates (AE), linear alkylbenzene sulfonates (LAS) and alcohol ethoxysulfates (AES). This paper discusses a systematic study of the effect of these and other potential surfactants on the stability of enzymes in laundry liquids. The focus of this work has been to begin elucidating surfactant structural features which minimize enzyme deactivation in aqueous media.

EXPERIMENTAL

Surfactants and Enzymes Used

Table I lists the anionic and nonionic surfactants used in these enzyme stability studies. The anionics were composed of four hydrophilic types:

- Sodium sulfonates (C_{12} LAS [Witconate® 1260, Witco Chemical Corp.], C_{1416} AOS [Bioterge® AS40, Stepan Chemical Co.], SXS [Witconate® SXS, Witco Chemical Corp.] and C_{1318} PS [Hostapur® SAS 60, American Hoechst Corp.]) in which the sulfonate moiety is bonded to a carbon atom of the hydrophobe.
- Sodium alcohol ethoxysulfonates (AE 25-3 sulfonate and AE 25-16 sulfonate) in which the sulfonate moiety is bonded to a carbon atom of the hydrophile. These are not commercial products and were prepared in the laboratory quantities by nucleophilic substitution reactions in which Na_2SO_3 was reacted with the appropriate alcohol ethoxysulfate.
- Sodium alcohol sulfates (C_{1215} AS [prepared by SO_3 sulfation of Neodol® 25 alcohol manufactured by Shell Chemical Co., followed by neutralization with NaOH], SDS [Aldrich Chemical Co.]) in which an oxygen atom of the sulfate moiety is bonded to a carbon atom of the hydrophobe.
- Sodium and ammonium alcohol ethoxysulfates (AE 25-3S [Neodol 25 ethoxysulfates, Shell Chemical Co.], AE 25-3A [Neodol 25 ethoxysulfates, Shell Chemical Co.]) in which an oxygen atom of the sulfate moiety is bonded to a carbon atom of the hydrophile.

The nonionic surfactants were alcohol ethoxylates (Neodol 25 ethoxylates, Shell Chemical Co.) with varying hydrophobic and hydrophilic chain lengths.

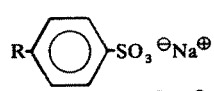
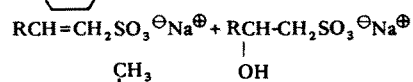
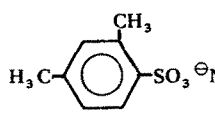
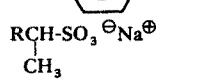
Enzymes used in these studies were composed of two liquid proteases (Esperase® 8L, Novo Laboratories, Inc., and Maxacal® L300,000, G.B. Fermentation Industries, Inc.) and two liquid amylases (Termamyl® 120L, Novo Laboratories, Inc., and Maxamyl® WL7000, G.B. Fermentation Industries, Inc.) having the activities listed in Table II.

Enzyme Assays

Protease assays were based on a Novo modification of a literature method (6). In this modification, the protease is allowed to hydrolyze azocasein for 30 min at 40 C. Undigested protein is precipitated with trichloroacetic acid, and the quantity of digested products is determined by spectrophotometry using a calibration curve obtained with

TABLE I

Surfactants Used in Enzyme Stability Studies

Surfactants	Source	Active matter, %w	General chemical structure
Anionics			
C_{12} LAS (C_{12} linear alkylbenzene sulfonate)[a]	Witco	33	
C_{14-16} AOS (C_{14-16} alpha olefin sulfonate)[a]	Stepan	39	
SXS (xylene sulfonate)[a]	Witco	40	
C_{13-18} PS (C_{13-18} paraffin sulfonate)[a]	Hoechst	64	
AE 25-3 Sulfonate (C_{12-15} alcohol 3EO sulfonate)[a]	Shell[b]	67	$RCH_2O(CH_2CH_2O)_2CH_2CH_2SO_3^{\ominus}Na^{\oplus}$
AE 25-16 Sulfonate (C_{12-15} alcohol 16EO sulfonate)[a]	Shell[b]	71	$RCH_2O(CH_2CH_2O)_{16}CH_2CH_2SO_3^{\ominus}Na^{\oplus}$
SDS (dodecyl sulfate)[a]	Aldrich	98	$ROSO_3^{\ominus}Na^{\oplus}$
C_{12-15} AS (C_{12-15} alcohol sulfate)[a]	Shell[b]	32	$ROSO_3^{\ominus}Na^{\oplus}$
AE 25-3S (C_{12-15} alcohol 3EO sulfate)[a]	Shell	60	$RO(CH_2CH_2O)_2CH_2CH_2OSO_3^{\ominus}Na^{\oplus}$
AE 25-3A (C_{12-15} alcohol 3EO sulfate)[c]	Shell	60	$RO(CH_2CH_2O)_2CH_2CH_2OSO_3^{\ominus}NH_4^{\oplus}$
Nonionics			
AE 91-6 (C_{9-11} alcohol ethoxylate - 6EO)	Shell	100	$RO(CH_2CH_2O)_6H$
AE 25-7 (C_{12-15} alcohol ethoxylate-7EO)	Shell	100	$RO(CH_2CH_2O)_7H$
AE 25-9 (C_{12-15} alcohol ethoxylate-9EO)	Shell	100	$RO(CH_2CH_2O)_9H$
AE 25-12 (C_{12-15} alcohol ethoxylate-12EO	Shell	100	$RO(CH_2CH_2O)_{12}H$
AE 25-18 (C_{12-15} alcohol ethoxylate - 18EO	Shell[b]	100	$RO(CH_2CH_2O)_{18}H$

[a]As sodium salt.

[b]Not produced commercially.

[c]As ammonium salt.

TABLE II

Liquid Enzymes Used in Enzyme Stability Studies

Type	Source	Activity
Protease	Novo	8 KNPU[a]/g
Protease	G.B. Fermentation	300,000 ADU[b]/g
Amylase	Novo	120 KNU[c]/g
Amylase	G.B. Fermentation	7,000 TAU[d]/g

[a]KNPU = Kilo Novo Protease Units, a Novo Industries designation for protease activity.

[b]ADU = Alkaline Delft Units, a G.B. Fermentation Industries designation for protease activity.

[c]KNU = Kilo Novo Units, a Novo Industries designation for amylase activity.

[d]TAU = Thermal Amylase Units, a G.B. Fermentation Industries designation for amylase activity.

a protease standard.

Alpha amylase assays were obtained using a Novo procedure. In this procedure, a cross-linked, water-insoluble, blue-colored starch polymer is used as substrate. This starch polymer is mixed with bovine serum albumin and a buffer substance and tableted. After suspension in water, the starch is hydrolyzed by the alpha amylase, giving soluble, blue-colored fragments. The absorbance of the resulting blue solution, measured spectrophotometrically at 620 nm, is a function of the alpha amylase activity.

Enzyme assays described above had a precision of ±8% of the amount present.

Enzyme Detergency Tests

Enzyme Test Cloths. Reflectance swatches—EMPA 116 cotton swatches stained with blood, milk and ink purchased from Testfabrics, Inc. Reflectances were read before and after washing, using the Y-scale of a Gardner XL-23 Colorimeter.

Radiolabeled blood—Permanent press polyester-cotton swatches were soiled with rabbit blood containing ^{59}Fe in the hemoglobin. The ^{59}Fe was incorporated by administering intravenously a solution of ^{59}Fe-ferrous citrate (1 mCi, 37.6 μCi/mg of ^{59}Fe) in 1 ml of a 1% aqueous citric acid solution (purchased from New England Nuclear, Boston, Mass.) until the specific radioactivity of the blood reached 0.25 μCi/ml. Radioactivity levels were monitored in whole blood and on fabric before and after washing, using a Beckmann Gamma 8000 gamma counter. A more complete description of the use of this radiolabeled blood will be presented in a future publication.

Washing tests were performed in a Terg-O-Tometer using 1.0 g/l of liquid laundry detergent in 500 ml H_2O containing 150 ppm total water hardness (calculated as $CaCO_3$ containing a Ca/Mg molar ratio of 3/2). Washwater temperature was 38 C. Two soiled swatches were deployed in each Terg-O-Tometer beaker, and all experiments were performed in duplicate. Least significant differences between any two average values at the 95% confidence level (LSD_{95}) were determined using a computer program which calculated variances and utilized a 2-tailed t-test to determine the LSD.

Formulations

Formulations were prepared using surfactants, ethyl alcohol, stabilizers where indicated, and H_2O buffered to pH levels indicated using appropriate quantities of 0.1 molar tris-(hydroxymethyl) aminomethane and 0.1 molar HCl.

Formulations for stability testing of enzymes were placed in a constant temperature water bath at 37 C and aliquots removed for enzyme assays at the times indicated.

RESULTS AND DISCUSSION

Stability of Enzymes

A comparison of the stabilities of the protease and amylase enzymes used in these studies is shown in Table III at two pH levels using a laundry liquid containing 30% of a 3/1 AE/AES surfactant system. As shown, the proteases showed essentially equivalent stabilities at both pH levels, while one of the amylases provided somewhat greater stability in this laundry liquid system than the other. The most stable of these enzymes was generally used in these studies.

TABLE III

Comparison of Stabilities of Protease and Amylase[a] from Different Commercial Sources

Enzyme	pH	% Enzyme stability, 37 C/14 days
Protease 1	7.5	79
Protease 1	9.0	88
Protease 2	7.5	84
Protease 2	9.0	86
Amylase 1	7.5	57
Amylase 1	9.0	64
Amylase 2	7.5	44
Amylase 2	9.0	33

[a]Formulation: AE 25-7, 22.5%; AE 25-3S, 7.5%; ethyl alcohol, 10%; enzyme 1.0%; H_2O (pH = 7.8), 59%.

Effect of Initial Protease Concentration on Stability

Since laundry liquids with varying initial enzyme concentrations were used in these studies, a brief investigation on the effect of initial protease concentration on protease stability was determined. The results plotted in Figure 1 indicate that % protease stability is not dependent on initial protease concentrations in the 0.25-5.0% range.

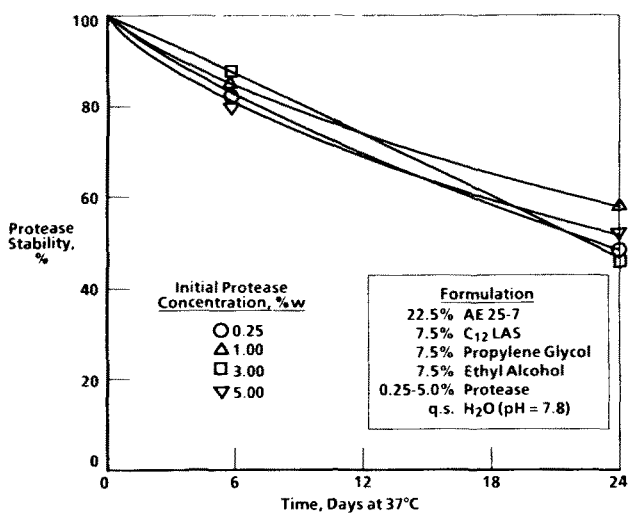


FIG. 1. Stability of protease in laundry liquids as a function of initial protease concentration.

Protease Stability in Anionic Surfactant Systems

Protease stability in the presence of 30% anionic surfactants formulated into a laundry liquid formulation are shown in Table IV. The use of a single surfactant in these formulations is not representative of commercial laundry liquids where nonionic/anionic surfactant blends are used. Also,

TABLE IV

Protease Stability in Presence of Anionic Surfactants[a]

Surfactant	% Protease stability at 37 C	
	3 days	14 days
C_{12} LAS	0	–
C_{14-16} AOS	0	–
SXS	0	–
C_{15-17} PS	0	–
AE 25-3 Sulfonate	39	29
AE 25-16 Sulfonate	0	–
SDS	0	–
C_{12-15} AS	0	–
AE 25-3S	95	88
AE 25-3A	44	19

[a]Formulation: surfactant, 30%; ethyl alcohol, 10%; protease, 1.0%; water buffered to pH - 7.8, 59%.

these formulations did not contain enzyme stabilizers. However, they served the purpose of assessing the relative capabilities of surfactants to provide enzyme stability. Stability data using more realistic formulations containing surfactant blends and stabilizers are discussed below.

The data listed in Table IV show that sulfonate-containing surfactants strongly deactivate protease. Results with the two alcohol ethoxysulfonates suggest that there may be a polyoxyethylene chain length which provides optimal enzyme stability for these types of surfactants, since AE 25-3 sulfonate provided some protease stability while AE 25-16 sulfonate provided none.

The two alcohol sulfates, SDS and C_{1215} AS, also were strongly deactivating toward protease in line with data in the literature (4,5) for this type of surfactant.

The only anionic tested which provided high levels of protease stability was AE 25-3S, the sodium salt of C_{12-15} alcohol 3 EO sulfate. Apparently, the intervention of 3 EO units between the alcohol and sulfate moieties produces an anionic surfactant which does not deactivate protease. The mechanism of enzyme deactivation and protection against deactivation in the presence of these surfactants currently is not understood, but may involve the size and configuration of surfactant micelles which entrap the enzymes in protective or non-protective environments (4).

Interestingly, AE 25-3A, in which the sodium ion has been replaced by ammonium ion, provides considerably poorer protease stability compared to AE 25-3S.

Protease Stability in Alcohol Ethoxylate Surfactant Systems

Table V lists protease stability data for laundry liquids containing alcohol ethoxylates. These data show that alcohol ethoxylates having varying hydrophobic and hydrophilic chain lengths provide good protease stabilities in these liquid systems. There does not appear to be an appreciable effect of hydrophobe or hydrophile chain lengths, although alcohol ethoxylates with EO chain length from 12-18 may afford slightly less enzyme stability than those having EO chain lengths from 6-9.

Protease Stability in Surfactant Blends

Most commercial laundry liquids contain blends of alcohol ethoxylates with either alcohol ethoxysulfates or linear alkylbenzene sulfonates. Table VI lists protease stability data using 30% surfactant formulations in which the nonionic, AE 25-7, is replaced systematically with increasing levels of anionic. As shown, at all levels of replacement studied, C_{12} LAS provided considerably poorer enzyme stability than

TABLE V

Protease Stability in Presence of Nonionic Surfactants[a]

Surfactant	% Protease stability at 37 C	
	3 days	14 days
None	34	0
AE 91-6	96	81
AE 25-7	100	86
AE 25-9	100	87
AE 25-12	92	76
AE 25-18	100	75
Propylene glycol	100	100

[a]Formulation: surfactant, 30%; ethyl alcohol, 10%; protease, 1.0%; water buffered to pH = 7.8, 59%.

TABLE VI

Protease Stability in Presence of Surfactant Blends[a]

Surfactant blend	% Protease stability at 37 C	
	1 day	7 days
AE 25-7	88	76
AE 25-7/C_{12} LAS = 3/1	76	19
AE 25-7/C_{12} LAS = 1/1	19	–
AE 25-7/C_{12} LAS = 1/3	0	–
C_{12} LAS	0	–
AE 25-7/AE 25-3S = 3/1	100	100
AE 25-7/AE 25-3S = 1/1	93	90
AE 25-7/AE 25-3S = 1/3	100	100
AE 25-3S	100	90

[a]Formulation: surfactants, 30%; ethyl alcohol, 10%; protease, 1.0%; water buffered to pH = 7.8, 59%.

AE 25-3S. The effect of increasing the C_{12} LAS content was to more rapidly deactivate protease. Increasing the AE 25-3S content had no effect on protease stability in this test with 90-100% stability achieved at all levels of AE 25-3S replacement.

Effect of Formulation pH on Enzyme Stability

Figures 2 and 3 show the effect of formulation pH on protease and amylase stabilities, respectively, using a formulation containing AE 25-7 and AE 25-3S as the surfactant system and pH levels of 5, 7.5 and 9. Unbuilt commercial U.S. laundry liquids generally have pH levels ranging from 7-9. As shown, there were no appreciable differences in both protease and amylase stabilities at pH levels of 7.5 or 9 using these surfactant systems. However, protease and amylase stabilities were extremely poor at a pH of 5. The trend toward lower enzyme stabilities with decreasing pH in the pH region studied is well known (7).

Effect of Surfactant Type and Concentration on Enzyme Stability

Figures 4 and 5 show the effect of total surfactant concentration and anionic type on protease and amylase stabilities, respectively. Surfactant levels ranged from 20-40% in 3/1 AE 25-7/anionic systems where the anionic was either C_{12} LAS or AE 25-3S. As shown in Figure 4 for protease stability, surfactant systems containing AE 25-3S provided essentially equivalent and high protease stabilities over the 20-40% surfactant concentrations studied. In contrast, the C_{12} LAS-containing systems provided much poorer protease stabilities, which decreased as the level of LAS increased.

The effect of these surfactant systems on amylase sta-

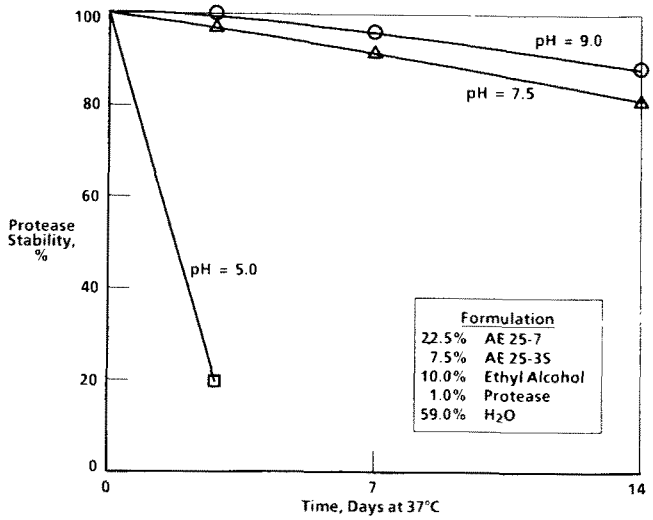


FIG. 2. Effect of pH on stability of protease in laundry liquids containing AE and AES.

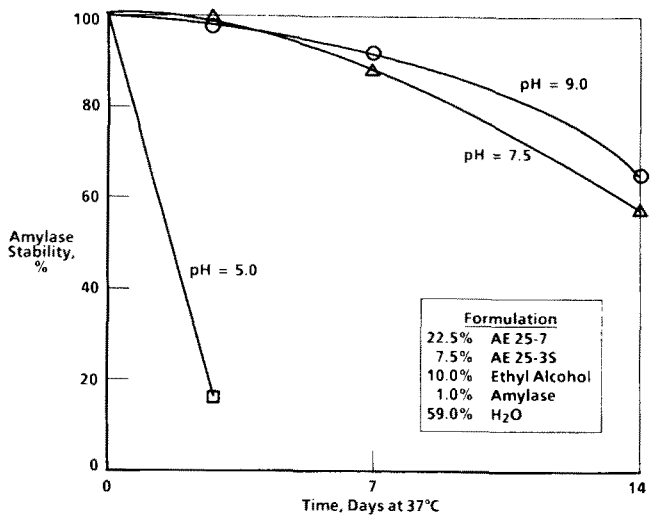


FIG. 3. Effect of pH on stability of amylase in laundry liquids containing AE and AES.

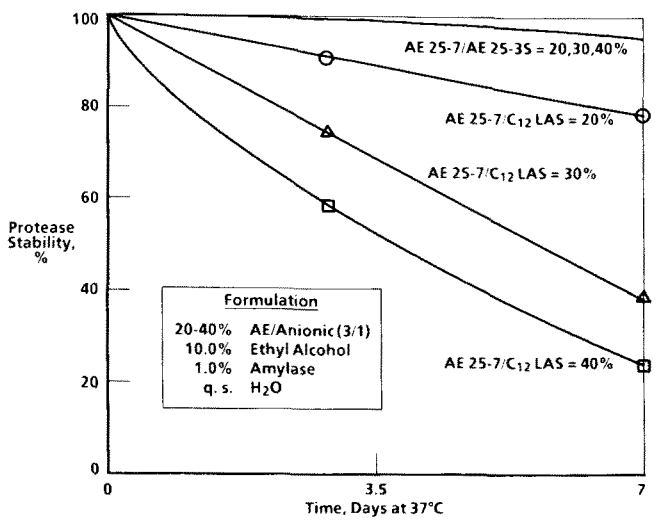


FIG. 4. Effect of surfactant type and concentration on stability of protease in laundry liquids.

bilities is shown in Figure 5. These results show much greater amylase stabilities using surfactants systems containing AE 25-3S than C_{12} LAS. However, with the systems containing AE 25-3S, there appears to be a slight amylase deactivating effect, because there is a downward trend in stability with increasing AE 25-7 and AE 25-3S concentrations.

Stabilized Versus Unstabilized Laundry Liquids

The use of polyols and lower aliphatic acid salts like formate and acetate to stabilize enzymes in laundry liquids has been described recently in a number of patents and patent applications (8-12). A brief study was made of the effect of protease stability of propylene glycol and sodium formate, two of the stabilizers mentioned in these patents. Surfactant systems contained 3/1 AE 25-7/anionic blends at total surfactant levels of 30%. C_{12} LAS and AE 25-3S were compared in both stabilized and unstabilized systems. As shown in Figure 6, stabilized systems were less deactivating than unstabilized systems with the effect of stabilizers more pronounced for the LAS-containing systems. However, unstabilized AE 25-3S systems afforded as much enzyme protection as C_{12} LAS in stabilized systems.

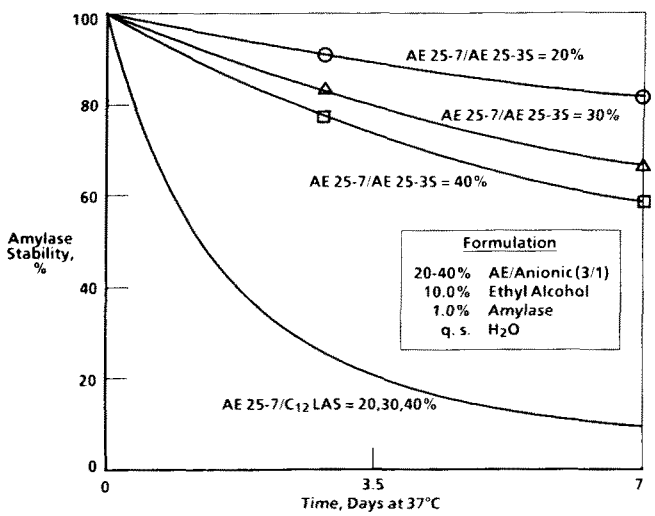


FIG. 5. Effect of surfactant type and concentration on stability of amylase in laundry liquids.

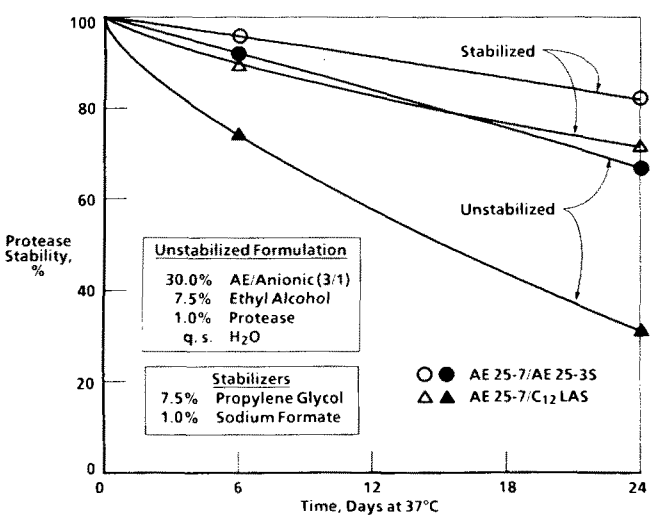


FIG. 6. Effect of AES and LAS on protease stability using stabilized and unstabilized laundry liquids.

Figure 7 shows protease stability in commercial enzyme-containing laundry liquids. As shown, the liquids containing alcohol ethoxylates and alcohol ethoxysulfates provided greater protease stability than those liquids in which LAS was one of the components–in line with the results described above.

Detergencies of Protease-Containing Liquids

The results of a brief study comparing the detergency performance of laundry liquids containing levels of protease varying from 0-2% are shown in Table VII using radiolabeled blood and EMPA 116. The radiolabeled swatches were evaluated by both radiotracer and reflectance techniques. As shown, the radiotracer and reflectance methods gave similar results in showing the effect of protease on proteinaceous soil detergency. The radiotracer method appears to have promise in being more discriminating than reflectance methods for distinguishing effects at varying protease levels.

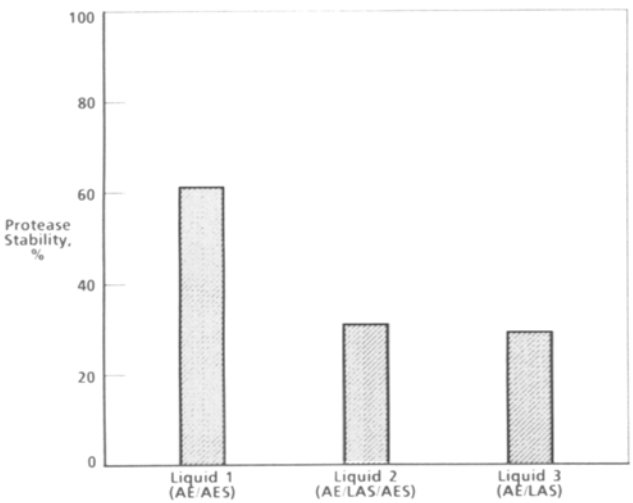


FIG. 7. Protease stability of commercial laundry liquids stored at 37 C for 24 days.

TABLE VII

Detergencies of ^{59}Fe Blood Stained Swatches

Formulation	%w Protease	Detergency %w Soil removed[a]	Detergency ΔR^b	Detergency ΔR^c
1[d]	0	26	2.2	14.2
1[d]	0.5	29	4.0	22.7
1[d]	1.0	31	4.5	21.4
1[d]	2.0	34	5.1	23.7
	LSD_{95}	3.1	1.0	1.3

[a]By scintillation counting ^{59}Fe before and after washing.
[b]By reflectance measurements before and after washing ^{59}Fe swatch.
[c]By reflectance measurements before and after washing EMPA 116.
[d]Formulation: AE 25-7, 22.5%; C_{12} LAS, 7.5%; ethyl alcohol, 7.0%; protease, 0-2.0%; H_2O (pH = 7.8), q.s.

Effects of Washwater pH on Proteinaceous Soil Removal

Figure 8 shows effects of washwater pH on EMPA 116 detergency using laundry liquid formulations in the presence and absence of protease. As shown, in the absence of protease, detergency increases moderately as washwater pH increases from 6-10, reaching a maximum level at approximately pH 8-9. In the presence of protease, however, there

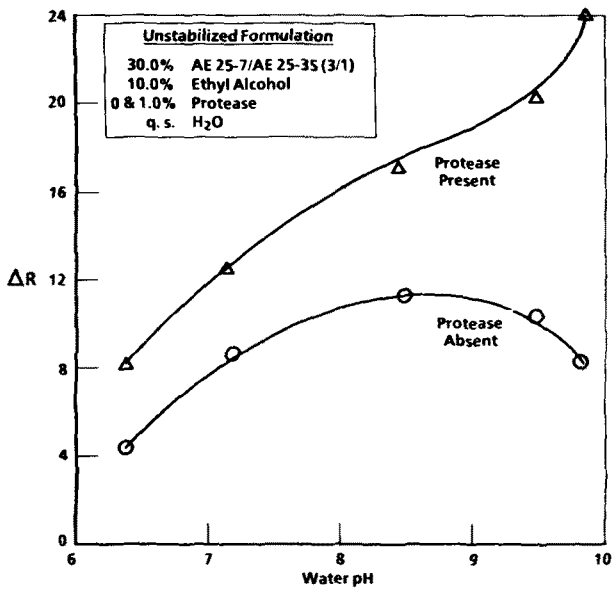


FIG. 8. EMPA 116 detergency as a function of washwater pH and protease.

is a much larger detergency increase as pH increases from 6-10, with no maximum observed in this pH range. These results are in agreement with those reported by Cayle using a different protease (13). The pH effect on soil removal with protease is largely a result of increased enzyme activity at the higher pH levels used in this study.

Stability of Protease in Laundry Liquids as Determined by EMPA 116 Detergency

Figure 9 shows EMPA 116 detergency as a function of protease remaining after accelerated testing at 37 C. As shown, EMPA 116 has the capability of distinguishing between formulations where protease stability varies from zero to 100%, with poor discrimination in the 25-75% stability range. The radiolabeled blood swatch will be investigated in future studies in an attempt to discriminate between varying stability levels of protease in this stability range.

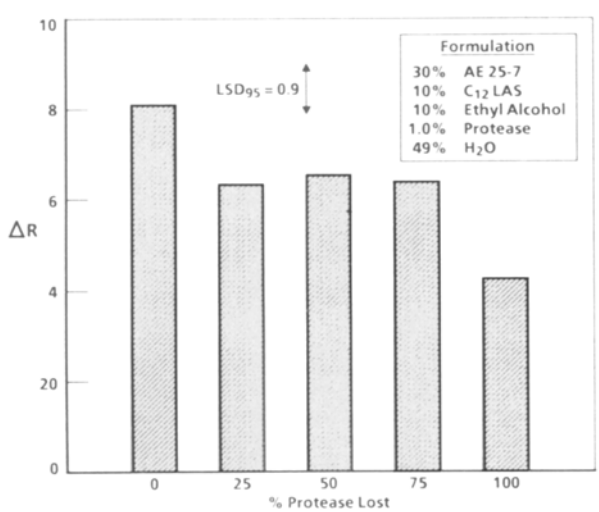


FIG. 9. EMPA 116 detergencies using enzyme-based laundry liquids after stability tests at 37 C.

ACKNOWLEDGMENTS

The authors are grateful to L.S. Wright for preparation of enzyme formulations and detergency data and to S.L. Rockey for enzyme assays.

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[Received June 10, 1984]

Multi-Functional Polyacrylate Polymers in Detergents[1]

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ABSTRACT

Alkali metal salts of polyacrylic acids are water-soluble, multi-functional polyelectrolytes which exhibit a variety of solution properties useful in laundry and dishwashing detergents. This paper describes a number of studies carried out to identify the multi-functionality of polyacrylates under simulated detergent use conditions. Solution properties of several commercially available polyacrylates, with average molecular weight ranging from about 2500 to 250,000, are presented. These include: adsorption onto model particulate soil materials and fabrics, particulate soil and lime-soap dispersancy, sequestration of calcium, magnesium and ferric ions, calcium carbonate precipitation inhibition, buffer action and detergency. Where appropriate, these solution properties are compared with those of commonly used non-polymeric detergent ingredients.

INTRODUCTION

Alkali metal salts of polyacrylic acids are water-soluble, multi-functional polyelectrolytes exhibiting a variety of solution properties useful in laundry and dishwash detergent compositions. These polyacrylates contain anywhere from 10 to upwards of 4000 repeating monomer units having the structural formula: $-CH_2 \cdot CH(COO^-)-$. Historically, the use of sodium polyacrylates as thickeners and builders in synthetic detergents has been suggested (1) as early as in 1949. At about the same time, Edelson and Fuoss, (2,3) used sodium polyacrylates as model compounds in their basic studies illustrating the fundamental differences between such polyelectrolytes and simple electrolytes as sodium bromide. However, large scale commercial use of sodium polyacrylates in synthetic detergent compositions probably did not come into effect until almost two decades later, as is evident from recently published reviews (4,5) on patents literature. In spite of this growing industrial use of polyacrylates in both commercial and institutional cleaner products, the published literature on the diverse functional benefits they confirm upon the end-use performance of a compounded detergent product is, at best, scanty (6-9). This paper describes a number of experimental studies carried out to identify the multi-functional benefits of these specialty detergent additives under simulated detergent-use conditions, and the likely role played by polyacrylates in basic detergency mechanisms.

[1]Presented at the 75th Annual AOCS Meeting, Dallas, 1984.

EXPERIMENTAL PROCEDURES

Materials

Polyacrylic acids used in this study were selected from the range of commercial (BF Goodrich Chemical) materials, whose analytical characteristics are shown in Table I. These were converted to their corresponding sodium salts by neutralization with sodium hydroxide to pH 10.5 and were used without further purification. Polyacrylate concentrations given in this report are on dry polymer basis. Details on other materials and reagents are given under appropriate experimental procedures described below.

Adsorption Isotherms

Complete details of the method will be published elsewhere

TABLE I

Analytical Characteristics of Polymeric Polyacrylates

Trade name	Molecular weight (by GPC)		Total solids (%)	pH 1% aqueous solution
	Weight-average (M_w)	Number-average (M_n)		
Good-rite® K-752	2,100	1,000	63	3.1
Good-rite® K-732	5,100	2,100	50	2.8
Good-rite® K-XP10	5,500	2,000	40	7.6
Good-rite® K-XP11	20,000	5,300	40	9.1
Good-rite® K-XP18	60,000	14,000	35	10.0
Good-rite® K-722	170,000	21,000	37	3.3
Good-rite® K-702	240,000	39,000	25	3.0